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(54) Improved use of flow improvers.

(57) Friction loss in hydrocarbon fluids flowing through conduits is reduced by adding to said hydrocrbon fluids an effective amount of an ultrahigh-molecular-weight polyolefin having an inherent viscosity of at least 11.0 deciliters per gram, said polymer added to said hydrocarbons in the form of a solution containing less than 10.0 weight percent active material. When added in this form, reduction in friction loss is surprisingly much higher than for similar concentrations of polymer added to the hydrocarbons in a more highly concentrated form.

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IMPROVED USE OF FLOW IMPROVERS

This invention relates to the reduction of frictional pressure loss encountered in the transfer of liquids by fluid flow through the use of a flow improving or drag reducing substance. More specifically, this invention relates to an improved method of injecting such substances into conduits transferring liquids in order to reduce turbulent flow and to increase the effectiveness of the flow improver.

It is well known that when a fluid is pumped or otherwise caused to flow through a conduit under pressure, energy is expended as a result of friction, and a frictional pressure loss results. Such frictional pressure losses are particularly large under turbulent flow conditions, for example when the velocity of a liquid passing through a conduit is such that turbulent flow results, a large frictional pressure loss is encountered. This problem of high frictional pressure loss or pressure drop in the flow of liquids through a conduit is commonly encountered in industrial operations wherein hydrocarbon liquids are conveyed through pipelines at high fluid velocities.

In order to compensate for the frictional pressure loss encountered from the turbulent flow of such hydrocarbon liquids, considerable energy, generally in the form of pumping horsepower, must be expended. Thus, reduction of the frictional pressure loss and the flow of such hydrocarbon liquids brings about an advantageous reduction of horsepower requirements or alternatively an increased flow rate of a hydrocarbon liquids under the same pumping conditions.

The art is aware of these problems as is represented by U.S. Patent 3,692,676, which discloses a method of reducing friction loss when fluids a pumped through pipelines by adding a high molecular weight poly-alpha-olefin. This patent taught that such polymers reduce friction in the flowing liquid by reducing turbulence. A method of measuring performance of these polymers was defined as

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$$\% \text{ Drag reduction} = \frac{(\text{pressure drop}_{\text{diesel}} - \text{pressure drop}_{\text{polymer}})}{\text{pressure drop diesel oil}} \times 100$$

U.S. Patents 3,748,266 and 3,758,406 relate to methods and compositions for reducing frictional pressure loss in hydrocarbon flows. Reduction in pressure loss was accomplished by adding a homopolymer such as a polyisobutylene having an intrinsic viscosity between 2 and 10 deciliters per gram to allow a low total concentration of polymer to hydrocarbon of about 2.5 pounds per 1,000 gallons, respectively.

U.S. Patent 3,351,079 uses drag reducers comprising ethylene, propylene and butylene terpolymers having a molecular weight up to about 1 million and useful at concentrations of from 0.01 to about 0.3 weight percent.

U.S. Patent 3,493,000 discloses high molecular weight cis-polyisoprene, cis-polybutadiene and ethylene-propylene copolymers used at concentrations of about 40 parts per million. U.S. 3,559,664 relates to the addition of ethylene-propylene copolymers to hydrocarbon liquids at levels of about 300 parts per million by weight.

These references, while not exhaustive of the art in the area, generally represent such art. These references all deal with total concentration of drag reducing material in polymer and attribute various levels of drag reduction to such total concentration of polymers.

Drag reducing polymers currently in use are reputed to be useful at low levels, yet often in practice require higher levels in order to sufficiently reduce turbulent flow to a desirable extent. In view of the cost of these polymers, as well as the possible contamination effect if used in a finished product pipeline, it would be greatly advantageous to provide a method whereby such polymers are effective at lower concentrations, or in the alternative, provide much higher levels of drag reduction at equivalent concentrations in the flowing hydrocarbon fluid.

I have now discovered a method for reducing friction loss in hydrocarbon fluids flowing through conduits comprising adding to said hydrocarbon fluid an ultrahigh-molecular-weight

polymer having an inherent viscosity of at least 11.0 deciliters per gram, said high molecular weight polymer dissolved or suspended in a hydrocarbon diluent, wherein the polymer is present in the diluent at a concentration of less than 10 percent by weight, based on the total weight of the diluent and the ultrahigh-molecular-weight polymer, and is placed into the flowing hydrocarbon fluid such that the total polymer concentration in the flowing hydrocarbon fluid ranges from about 0.01 to about 500 parts per million by volume.

It is necessary in the present invention that the ultrahigh-molecular-weight polymer have a inherent viscosity of at least 11.0 deciliters per gram as measured in a low polynuclear aromatic solvent (LPA) at a temperature of from about 77 to about 78°F, at a shear rate of 300 reciprocal seconds, and at a concentration of 0.10 g/100 ml.

25°C

Thus, in the process of the present invention the drag reducing mixture will contain less than 10 weight percent of an ultrahigh-molecular-weight poly-alpha-olefin. These poly-alpha-olefins can be homopolymers, copolymers, or terpolymers prepared by contacting alpha-olefins containing from 2 to 30 carbon atoms with a polymerization catalyst. The catalyst and method of preparing these polymers is not critical other than the inherent vicosities of the resulting polymers must be greater than 11.0 deciliters per gram at a shear rate of 300 sec^{-1}, and that these materials be substantially soluble in the hydrocarbon liquid in order to reduce turbulent flow. It is preferred in the practice of the present invention to have a polymer content of from about 2 to about 6 weight percent at an inherent viscosity of from about 12.0 to about 15.0 deciliters per gram for maximum effectiveness.

The drag reducing polymer, once prepared, is placed in a suitable carrier substance. These materials are usually inactive hydrocarbon solvents. Representative but non-exhaustive examples of such materials are straight chain aliphatic compounds or branched hydrocarbons such as ethane,

propane, isobutane, butane, pentane, hexane, heptane, or isooctane, octane. Also useful are alicyclic hydrocarbons such as cyclohexane, methylcyclopentane, and tetralene. Aromatic hydrocarbons can also be used as represented by benzene, toluene, and xylene. Mixtures and analogues of these compounds are also useful as represented by MOLEX (trademark of Universal Oil Products) raffinate, which is a complex mixture of branched aliphatic, cyclic aliphatic, aromatic and trace amounts of unbranched aliphatic hydrocarbons. Likewise useful are low polynuclear aromatic solvents. Further, the hydrocarbon diluent can be an alpha-olefin.

It should be noted in the context of the present invention that when the alpha-olefin drag reducing polymer contains significant amounts of lower olefins such as ethylene and butene, a small but significant amount of hydrocarbon-insoluble material may be produced. This hydrocarbon-insoluble material will be apparent in the diluted mixture prepared for injection into the flowing hydrocarbon liquid, but such materials will dissolve in the much larger volumes of the flowing hydrocarbon fluid. Therefore, in the context of the present invention, these materials may be dissolved or suspended or a combination of these physical states when injected into the pipeline. In either case, the term "suspended" as used in this specification and claims will indicate that the polymer can be totally or partially dissolved, with any undissolved polymer suspended in the hydrocarbon medium.

In any event, once in this state, the material is injected into a conduit containing flowing hydrocarbons. In contrast to materials which are produced at lower inherent viscosities, or those having high inherent viscosities which are injected at concentrations of 10% by weight or more, the instant invention shows a surprising increase in drag reduction effectiveness.

The hydrocarbon liquids in which the additive of this invention is effective include oleaginous or petroliferous liquids as well as emulsions, suspensions, and dispersions thereof. For example crude oil, refined petroleum products

such as kerosene, pale oil, diesel oil, fuel oil, asphalt, etc., water-in-oil emulsions, surfactants and the like. Where the hydrocarbon liquid is a hydraulic fracturing fluid, it may also contain solid particulate matter such as sand as a propping agent, a fluid loss control additive and other materials commonly added to fracturing fluids.

In the preferred embodiment of the present invention the drag reducing polymer is formed from olefins containing from 5 to 20 carbon atoms which optionally can contain from about 0.01 to about 20% by weight of ethylene or propylene, and up to 50% butene-1 comonomer. Polymers so produced will have an inherent viscosity of from about 11.5 to about 15.0 and will be placed in the flowing hydrocarbon fluid at a concentration of from about 0.1 to about 3.5% by weight of the diluent or suspending agent.

The invention is more concretely described with reference to the examples below wherein all parts and percentages are by weight unless otherwise specified. The examples are provided to illustrate the present invention and not to limit it.

Example 1

A catalyst slurry was prepared by mixing under an inert atmosphere of dry argon, 0.104 grams of $TiCl_3$.AA (Type 1.1 catalyst from Stauffer Chemical Company), 0.36 milliliters (ml) of dried and deoxygenated Molex raffinate (obtained from Conoco Chemicals; Molex is a trademark of Universal Oil Products). This mixture was stirred for approximately 2 minutes in a dry box. Di-n-butylether (60 microliters, dried and degassed) was added. The mixture was then stirred vigorously for 15 minutes in a small vial equipped with a microstir-bar. This mixture was then transferred to a gas-tight syringe. The vial was washed with 10 milliliters of low polynuclear aromatic solvent (LPA) and the wash material added to the same syringe.

Example 2

The catalyst of example 1 was used in the preparation of a drag reducing polymer.

A mixture of 189 ml of dried and deoxygenated low polynuclear aromatic solvent, 3.6 ml of diethylaluminum chloride (DEAC, purchased from Texas Alkyls as a 10% solution in heptane) and 41 ml of dried and degassed decene-1 was placed into a clean, dry 1-quart bottle under an atmosphere of dry argon. The mixture was cooled to -7°C and agitated in a shaker bath at 500 revolutions per minute (rpm).

The catalyst mixture described in example 1 was added to initiate the polymerization. The mixture became thick. After 3 hours the bottle was removed from the temperature bath. A thermometer was placed into the center of the viscous material, recording a temperature of 6°C. The polymerization was, therefore, semi-adiabatic due to the insulation effect of the poly(decene-1) mixture.

Approximately 1.7 ml of methanol was added to deactivate the catalyst. The polymer mixture was stabilized with about 0.01 weight percent butylated hydroxy toluene (BHT) as an antioxidant. The weight of polymer produced was determined by pouring 84.9 grams of the deactivated polymer mixture into 400 ml of isopropyl alcohol with sufficient mixing to precipitate a viscous material containing poly(decene-1). The substance was washed with an additional 400 ml of isopropyl alcohol, filtered and washed with 400 ml of methanol to remove catalyst residue. The poly(decene-1) was collected by vacuum filtration and dried in a vacuum oven overnight to produce 4.2075 grams of polymer. The polymer solution thus contained 4.95% poly(decene-1). This polymer solution was used to determine the inherent viscosity of dissolved polymer. The inherent viscosity ~~method~~ was determined in IPA solvent at 77.5 ± 0.5°F using a Cannon-Ubbelohde four bulb shear dilution viscometer at a shear rate of 300 reciprocal seconds.

Example 3

A calibrated Cannon-Ubbelohde Four-Bulb Shear Dilution Viscometer is used to measure the flow time for both solvent and polymer samples. Inherent viscosity values are calculated for each of the four bulbs. These calculated

values are plotted as a function of shear rate, and the resulting plot is used to obtain the inherent viscosity at a shear rate of 300 sec^{-1}.

Approximately 0.5 gm of the drag reducer material (for example, a solution containing 4.95 weight percent poly(decene-1) in LPA solvent as obtained in Example 2) is placed into a clean, dry Erlenmeyer flask equipped with a ground glass stopper. LPA solvent is added to generate a concentration of 0.10 gm polymer/100 ml. The stoppered flask is placed on a magnetic stirrer and stirred until dissolution is completed. The stirring speed is set to minimize shear degradation of the polymer. Shear degradation will produce an anomalously low inherent viscosity value.

LPA solvent (10ml) is placed into the viscometer, and the viscometer is immersed into a water bath. The system is allowed to equilibrate for at least 20 minutes.

The efflux time for each bulb is determined according to the procedure supplied with the viscometer.

The viscometer is cleaned and dried by flushing with hexane, then with acetone. The efflux time for the sample solution is measured following the same procedure as used for the LPA solvent.

The inherent viscosity for reach bulb is calculated using the following equations:

Relative Viscosity $(\eta_{rel}) = t_{soln.}/t_{solvent}$

where,

$t_{soln.}$ = efflux time of the solution

$t_{solvent}$ = efflux time of the solvent.

Inherent Viscosity $(\eta_{inh}) = l_n \eta_{rel/C}$ where,

C = concentration in g/dl

The shear rate for each bulb is calculated using the relationship: Shear Rate $(\dot{\gamma}) = K/t_{soln.}$ where,

K = shear rate constant.

A plot of shear rate versus inherent viscosity is made. The inherent viscosity at a shear rate of 300 sec^{-1} is then determined.

Examples 4 through 8

The instant invention was demonstrated in a pipeline. A polymer solution containing 10.8% poly(decene-1) with an inherent viscosity of 11.8 dl/gm at a shear rate of 300 sec^{-1} was made using a procedure similar to Examples 1 and 2. Conditions and quantities were adjusted to yield 10.8% polymer. Approximately 12 weight percent decene-1 was charged into the polymerization vessel. The polymerization was termined with alcohol. The weight percent polymer content was determined by the procedure set forth in Example 2. The inherent viscosity of the dissolved polymer was determined by the four bulb viscometer procedure as described in Example 3.

The 10.8% polymer solution was diluted with LPA to yield a 5.95% and a 0.94% polymer solution. A Pfaudler mixer was used to conduct the dilution. The agitator was set at a low mixing speed to prevent shear deterioration of the polymer.

The effectiveness of the drag-reducing materials so produced was tested in the Kingfisher pipeline in Oklahoma. This crude oil pipeline runs from the Kingfisher pump station near Hennessey, Oklahoma, to a tank storage area in Orlando, Oklahoma. The inner diameter of the pipeline is 8.24 inches and the total length of 28.3 miles. Drag reducer performance was evaluated in the first 7.4 mile section of the pipeline from the Kingfisher pump station. Dual-piston positive displacement pumps were used to maintain pipeline flow. The drag reducers were injected directly into the 8.24 inch line downstream of the pump at Kingfisher. The crude oil flow rate during the tests was approximately 1,272 barrels per hour (BPH), which corresponds to a pipeline flow velocity of 5.3 ft/sec. As a control, a poly(decene-1) solution was prepared containing 6.10% polymer having an inherent viscosity of 9.5 dl/gm at a shear rate of 300 sec^{-1}.

Test results are set forth in Table 1, where examples 4 and 8 are control experiments, and examples 5, 6 and 7 demonstrate the present invention.

Table 1

Example	Weight Percent Polymer	Inherent Viscosity (dl/gm at 300 sec^{-1})	Polymer Injected into Pipeline(ppm)	Percent Drag Reduction
4	10.8	11.9	4.0	33
5	5.95	11.9	3.1	36
6	0.94	11.9	3.2	39
7	0.94	11.9	0.84	19
8	6.10	9.5	3.1	20

Control example 4 shows that injection of a 10.8 wt% 11.9 inherent viscosity material into the pipeline at approximately 4.0 ppm level of polymer content resulted in 33% drag reduction in the 7.4-mile section of pipeline. An 11.9 inherent viscosity material containing 5.95 wt% polymer and 0.94 wt% polymer resulted in much better drag reduction performance. Less polymer was required to yield greater drag reduction. Surprisingly, the 0.94 wt% material (example 6) was more effective than the 5.95 wt% material (example 5).

Examples 9 through 11

A test was carried out in the Brent pipeline system in the North Sea connecting Conoco's Murchison Platform and Shell's Dunlin-A platform. This connecting pipeling segment is 14.75-inches in diameter (ID) and 11.74 miles in length and carries crude oil production from the Murchison platform. The Murchison crude properties are:

API Gravity	38.5°
Viscosity, C_s	11.3 - 12.4 at 32°F 5.4 - 5.8 at 70°F 3.5 - 3.7 at 100°F

In these tests, three materials were employed. Comparative example 9 used a 10.8 wt% poly(decene-1) solution with an inherent viscosity of 11.9 dl/gm at a shear rate of 300 sec^{-1}. Example 10 used a 10.8 wt% material diluted to approximately 3.0 wt% polymer content in LPA solvent. Again, the dilution was conducted in a Pfaudler mixer under conditions which prevented shear degradation of the polymer.

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The inherent viscosity of the polymer was 11.9 dl/gm at a shear rate of 300 sec^{-1}. Example 11 used a drag reducer which contained approximately 10.5 wt% poly(decene-1) with an inherent viscosity of 9.5 dl/gm at a shear rate of 300 sec^{-1}.

Comparative example 11 was also conducted using a drag reducer with an inherent viscosity of 9.5 at a polymer content of 10.5% prior to injecting into the pipeline. Test results are presented in Table 2.

Table 2

Example	Weight Percent Polymer	Inherent Viscosity (dl/gm @ 300sec^{-1})	Polymer Injected into Pipeline (ppm)	Percent Drag Reduction	Calculated Flow Increase
9	10.8	11.9	10	19	12
10	3.0	11.9	10	50	46
11	10.5	9.5	22	17	11

The test results clearly show that performance of the 11.9 inherent viscosity material is greatly enhanced by dilution prior to injection into the pipeline. When comparing Example 9 with Example 10, a flow increase of about 46% was obtained using the diluted material (10), compared to only a 12% increase in flow using the concentrated drag reducer (9). Comparative examples 9 and 11 showed only 12% and 11% flow increase, respectively. There was a great deal of difference in inherent viscosities.

While theoretical in nature, and I do not wish to be bound thereby, it is believed that the higher weight concentration polymer solutions require longer times to go into solution with the crude oil. The higher inherent viscosity material, however, provides for better drag reduction if the material is dissolved in the crude oil. This hypothesis is supported by the data as evidenced by comparing example 5 with example 8.

While certain embodiments and details have been shown for the purpose of illustrating this invention, it will be apparent to those skilled in this art that various changes and modifications may be made herein without departing from the spirit or scope of the invention.

I claim:

CLAIMS:

1. A method for reducing friction loss in hydrocarbon fluids flowing through conduits comprising adding to said hydrocarbon fluid a high molecular weight polymer having an inherent viscosity of at least 11.0 deciliters/gram suspended in a hydrocarbon diluent or suspending agent where the polymer is present in the diluent or suspending agent at a concentration of less than 10.0 weight percent when placed into the flowing hydrocarbon fluid and the total polymer concentration in the flowing hydrocarbon fluid ranges from about 0.01 to about 500 parts per million.

2. A method as described in claim 1 wherein the polymer molecular weight as measured by inherent viscosity in low polynuclear aromatic solvents at 77 to 78°F is at least 11.0 at a shear rate of 300 reciprocal seconds and the concentration of polymer prior to insertion is 5.0 weight percent or less of the hydrocarbon diluent or suspending agent.

3. A method as described in claim 2 wherein the polymer is a poly(alpha-olefin).

4. A method as described in claim 3 wherein at least half of the poly(alpha-olefin) polymer is formed from olefins containing from 5 to 20 carbon atoms.

5. A method as described in claim 4 wherein from about 0.01 to about 20% by weight of the poly(alpha-olefin) polymer is formed from ethylene or propylene.

6. A method as described in claim 5 wherein from 1 to about 50% by weight of the poly(alpha-olefin) is formed from butene-1 comonomer.

7. A method as described in claim 5 wherein the polymer placed in the flowing hydrocarbon fluid has an inherent viscosity of from about 11.5 to about 15.0.

8. A method as described in claim 6 wherein the polymer solution or mixture placed in the flowing hydrocarbon fluid has a polymer concentration of from about 0.1 to about 3.5% by weight of the diluent or suspending agent.

European Patent Office

EUROPEAN SEARCH REPORT

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Application number

EP 85 10 4038

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
X	GB-A-2 074 175 (ATLANTIC RICHFIELD) * Claims 1-3,5,10,11-18 * ---	1,3,4,6	C 10 L 1/16 F 15 D 1/00
X,D	US-A-3 559 664 (E.V. SEYMOUR) * Claims 1-3 * -----	1-3,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl 4)
			C 10 L F 15 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-12-1985	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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